



APPLICATION No.11/290346

[Title of the document] REQUEST FOR GRANT OF PATENT

[Pocket number] 51A26410-A

[Date submitted] October 12, 1999

[Submitted to] The Director General of the Patent Office

[International patent classification] B32B 27/00

[Inventor]

[Address] c/o Nagoya Plant, Toray Industries, Inc.

9-1, Oe-cho, Minato-ku, Nagoya-shi, Aichi Pref.

[Name] MATSUOKA, Hideo

[Inventor]

[Address] c/o Nagoya Plant, Toray Industries, Inc.

9-1, Oe-cho, Minato-ku, Nagoya-shi, Aichi Pref.

[Name] KOBAYASHI, Kazuhiko

[Applicant]

[Identification number] 000003159

[Address] 2-1, Nihonbashi-muromachi 2-chome, chuo-ku, Tokyo

[Name] Toray Industries, Inc.

[Representative] HIRAI, Katsuhiko

[Telephone number] 03-3245-5648

[Payment of fee]

[Prepayment book number] 005186

[Amount of payment] 21,000

[List of the documents submitted]

[Title of the document] Specification 1

[Title of the document] Abstract 1

[Necessity of proof] required



[Title of the document] Specification

[Title of the invention] A laminated structure

[Claims]

[Claim 1]

A laminated structure comprising at least one barrier layer of a resin composition consisting of (a) 5-80 vol% of polyolefin resin and (b) 95-20 vol% of polyphenylene sulfide resin, wherein the phase structure as observed by electron microscopy comprises (b) a continuous layer of said polyphenylene sulfide resin and (a) a distribution layer of said polyolefin resin.

[Claim 2]

A laminated structure according to claim 1 wherein said (a) polyolefin resin and (b) polyphenylene sulfide resin account for 55-80 vol% and 45-20 vol%, respectively.

[Claim 3]

A laminated structure comprising at least one barrier layer of a resin composition consisting of (a) 15-85 vol% of polyolefin resin and (b) 85-15 vol% of polyphenylene sulfide resin, wherein the phase structure as observed by electron microscopy comprises (b) polyphenylene sulfide resin and (a) polyolefin resin, both in the form of a virtually continuous layer.

[Claim 4]

A laminated structure comprising at least one barrier layer of a resin composition consisting of (a) 55-95 vol% of polyolefin resin and (b) 45-5 vol% of polyphenylene sulfide resin, wherein the phase structure as observed by electron microscopy comprises (a) a continuous layer of polyolefin resin and (b) a zonal distribution layer of polyphenylene sulfide resin.

[Claim 5]

A laminated structure according to any of claims 1-4 wherein said

(a) polyolefin resin is at least one selected from the group consisting of polyethylene; polypropylene; ethylene/ α -olefin copolymers; copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate; and copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate, with at least part of the carboxyl groups being modified into a metal salt.

[Claim 6]

A laminated structure according to any of claims 1-5 wherein the adjacent layer to either side of the barrier layer comprises a thermoplastic resin that is different from the resin that forms the barrier layer.

[Claim 7]

A laminated structure according to claim 6 wherein said thermoplastic resin that forms the adjacent layer is at least one selected from the group consisting of polyolefin resin, thermoplastic polyester resin, polyamide resin, polycarbonate resin, and ABS resin.

[Claim 8]

A laminated structure according to claim 6 wherein said thermoplastic resin that forms the adjacent layer is polyolefin resin, thermoplastic polyester resin, or polyamide resin.

[Claim 9]

A laminated structure according to claim 6 wherein an adhesive layer exists between the barrier layer and the adjacent layer.

[Claim 10]

A laminated structure according to any of claims 1-9 that is produced by coextrusion.

[Claim 11]

A laminated structure according to any of claims 1-9 that is in the form of a multilayer tube or a blow-molded multilayer hollow

article produced by coextrusion.

[Detailed description of the invention]

[0001]

[Technical field of the invention]

The present invention relates to a laminated structure with high moldability and good gas and fuel barrier properties. In particular, the invention relates to a laminated structure that comprises a barrier layer having a specific phase structure consisting of polyolefin resin and polyphenylene sulfide resin, and accordingly serves as good material for containers and piping for storage and transportation of oil, gasoline and other liquid chemicals, as well as packages and containers for foods and medical products.

[0002]

[Prior art]

For fuel tanks and engine oil tanks in automobiles, studies have been conducted actively to allow a shift from metal to plastics in view of their weight, moldability, design freedom, and handling properties. Such containers should be free of leakage of contents and entry of external air to ensure high safety, storage stability, and environmental pollution prevention. Though the most widely used plastic container materials are polyolefin type polymers including polyethylene and polypropylene, they do not have sufficient barrier properties against gasoline and specific types of oil, and cannot work effectively when used solely as material for fuel tanks and engine oil tanks in automobiles, and accordingly, they are usually used in the form of a laminated structure that comprises a barrier layer made of resin with good barrier properties.

[0003]

Polyamide resin (for instance, see Japanese Patent Laid-Open Publication (Kokai) SHO 58-220738) is one of the most widely used

resins to produce such a barrier layer. With the increasingly frequent use in recent years of so-called gasohol, a mixture of gasoline and alcohol, as automobile fuel, plastic containers produced by conventional techniques as described above have become unable to show sufficiently good barrier properties, and expectations are high for the development of improved techniques for production of high-performance barrier layers.

[0004]

Compared to these, polyphenylene sulfide resin (hereafter abbreviated as PPS resin) is known to have excellent barrier properties against gasoline, automobile engine oil and other liquid chemicals as well as water and carbon dioxide gas, and new structures comprising this resin have been proposed, including blow-molded hollow containers and tubes (as shown for instance in Japanese Patent Laid-Open Publication (Kokai) SHO 62-90216, SHO 61-255832, and HEI 3-32816) and laminated structures comprising a barrier layer made of a specific type of PPS copolymer and modified polyolefin resin HEI (as shown for instance in Japanese Patent Laid-Open Publication (Kokai) 6-190980). PPS resin, however, cannot achieve strong interlayer adhesion with other resins, and it is difficult to perform coextrusion and lamination with polyolefin type polymers, such as polyethylene and polypropylene, or other resins, or necessary to use expensive, special PPS polymers as main component, resulting in a limited scope of application.

[0005]

[Problems to be solved by the invention]

The main goal of the invention is to provide a laminated structure that serves to produce high-performance plastic containers with good barrier properties against gasohol, and more specifically, to provide a laminated structure with high moldability, interlayer

adhesiveness and toughness, in addition to high manufacturing stability and high cost performance.

[0006]

[Means of solving the problems]

Thus, to achieve the goal described above, the present inventors have carried out studies and found that production of a barrier layer from a resin composition consisting of polyolefin resin and PPS resin can be performed very effectively by forming a continuous PPS resin phase in the barrier layer, and more effectively by using it in combination with an adjacent layer with a specific structure, which serves to provide a laminated structure that meet the above-mentioned requirements.

[0007]

Thus, the present invention relates to: (1) a laminated structure comprising at least one barrier layer of a resin composition consisting of (a) 5-80 vol% of polyolefin resin and (b) 95-20 vol% of polyphenylene sulfide resin, wherein the phase structure as observed by electron microscopy comprises (b) a continuous layer of polyphenylene sulfide resin and (a) a distribution layer of polyolefin resin; (2) a laminated structure according to item (1) above, wherein said (a) polyolefin resin and said (b) polyphenylene sulfide resin account for 55-80 vol% and 45-20 vol%, respectively; (3) a laminated structure comprising at least one barrier layer of a resin composition consisting of (a) 15-85 vol% of polyolefin resin and (b) 85-15 vol% of polyphenylene sulfide resin, wherein the phase structure as observed by electron microscopy comprises (b) polyphenylene sulfide resin and (a) polyolefin resin, both in the form of a virtually continuous layer; and (4) a laminated structure comprising at least one barrier layer of a resin composition consisting of (a) 55-95 vol% of polyolefin resin and (b) 45-5 vol%

of polyphenylene sulfide resin, wherein the phase structure as observed by electron microscopy comprises (b) a continuous layer of polyphenylene sulfide resin and (a) a zonal distribution layer of polyolefin resin.

[0008]

The invention also relates to: (5) a laminated structure according to any of items from (1) to (4) above, wherein said (a) polyolefin resin is at least one selected from the group consisting of polyethylene; polypropylene; ethylene/ α -olefin copolymers; copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate; and copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate, with at least part of the carboxyl groups being modified into a metal salt; (6) a laminated structure according to any of items from (1) to (5) above, wherein the adjacent layer to either side of the barrier layer comprises a thermoplastic resin that is different from the resin that forms the barrier layer; (7) a laminated structure according to item 6 above, wherein said thermoplastic resin that forms the adjacent layer is at least one selected from the group consisting of polyolefin resin, thermoplastic polyester resin, polyamide resin, polycarbonate resin, and ABS resin; and (8) a laminated structure according to item (6) above, wherein said thermoplastic resin that forms the adjacent layer is polyolefin type resin, thermoplastic polyester resin, or polyamide resin.

[0009]

The invention further relates to: (9) a laminated structure according to item (6) above, wherein an adhesive layer exists between the barrier layer and the adjacent layer; (10) a laminated structure according to any of items from (1) to (9) above that is produced

by coextrusion; and (11) a laminated structure according to any of items from (1) to (9) above, that is in the form of a multilayer tube or a blow-molded multilayer hollow article produced by coextrusion.

[0010]

[Mode for carrying out the invention]

Good modes for carrying out the invention are described below. Useful polyolefin type resins to be used for component (a) of the laminated structure according to the present invention include homopolymers including polyethylene, polypropylene, polystyrene, polyacrylate, polymethacrylate, poly-1-butene, poly-1-pentene and polymethylpentene; ethylene/ α -olefin copolymer; homopolymers of vinyl alcohol esters; polymers produced by hydrolyzing at least part of a homopolymer of a vinyl alcohol ester; polymers produced by hydrolyzing at least part of a copolymer of ethylene and/or propylene, and a vinyl alcohol ester; copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate; copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate, with at least part of the carboxyl groups being modified into a metal salt; block copolymers of a conjugated diene and an aromatic vinyl hydrocarbon; and hydrides of said block copolymers.

[0011]

Among others, preferred ones include polyethylene, polypropylene, ethylene/ α -olefin copolymer, ethylene/(meth)acrylic acid copolymer, and ethylene/(meth)acrylic acid copolymer with at least part of the carboxyl groups being modified into a metal salt, ethylene/(meta)acrylic acid/(meta)acrylate copolymer, ethylene/(meta)acrylic acid/(meta)acrylate copolymer with at least part of the carboxyl groups being modified into a metal salt, of

which low, medium and high density polyethylene, polypropylene, and ethylene/ α -olefin copolymer are particularly preferred. There are no specific limitations on the structure of said polypropylene, and isotactic, atactic, and syndiotactic ones can be used appropriately. In addition to homopolymers, block and random copolymers consisting of 70 wt% or more propylene and other olefin components can be used.

[0012]

Said ethylene/ α -olefin copolymer refers to a copolymer of ethylene and one or more α -olefins with 3-20 carbon atoms, and said α -olefins with 3-20 carbon atoms include propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecen, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecen, 1-eicosen, 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene, 9-methyl-1-decene, 11-methyl-1-dodecen, 12-ethyl-1-tetradecene, and combinations thereof. Of these α -olefin-based copolymers, those comprising an α -olefin with 3-12 carbon atoms are preferred in terms of mechanical strength. In said ethylene/ α -olefin copolymers, α -olefins should preferably account for 1-30 mol%, more preferably 2-25 mol%, and further more preferably 3-20 mol%.

[0013]

Further, said copolymers may comprise one or more nonconjugated diene such as 1,4-hexadiene, dicyclopentadiene, 2,5-norbornadiene, 5-ethylidene norbornene, 5-ethyl-2,5-norbornadiene, and 5-(1'-propenyl)-2-norbornene.

[0014]

The unsaturated carboxylic acid used in said copolymers of propylene

and/or ethylene and an unsaturated carboxylic acid and/or an unsaturated carboxylate is either an acrylic acid or a methacrylate, or a mixture thereof, while the unsaturated carboxylate is a methyl ester, ethyl ester, propyl ester, butyl ester, pentyl ester, hexyl ester, heptyl ester, octyl ester, nonyl ester, or decyl ester of either of the above unsaturated carboxylic acids, or a mixture thereof, preferred copolymers being those produced from ethylene and a methacrylic acid and those produced from ethylene, a methacrylic acid and an acrylate.

[0015]

Moreover, for purposes of the present invention, said (a) polyolefin resin may be produced by modifying one of the above-mentioned polyolefin type resins with one or more derivative of an unsaturated carboxylic acid. The use of a modified polyolefin resin as described above leads to an increased compatibility compared to the original resin and enhanced controllability of the phase structure of the resulting resin composition, which serve to achieve good barrier properties, thus representing a preferred embodiment of the invention.

[0016]

Unsaturated carboxylic acid derivatives often used as modifier include acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, methyl maleic acid, methyl fumaric acid, masaconic acid, citraconic acid, glutaconic acid, metal salts of the foregoing carboxylic acids, methyl hydrogen maleate, methyl hydrogen itaconate, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, hydroxyethyl acrylate, methyl methacrylate, 2-ethylhexyl methacrylate, hydroxyethyl methacrylate, aminoethyl methacrylate, dimethyl maleate, dimethyl itaconate, maleic anhydride, itaconic anhydride, citraconic anhydride,

endo-bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid,
endo-bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride,
maleimide, N-ethylmaleimide, N-butylmaleimide, N-phenylmaleimide,
glycidyl acrylate, glycidyl methacrylate, glycidyl ethacrylate,
glycidyl itaconate, glycidyl citraconate, and
5-norbornene-2,3-dicarboxylic acid. Of these, preferred ones
include unsaturated dicarboxylic acids and their anhydrides, of
which maleic acid and maleic anhydride are particularly preferred.
[0017]

With no particular limitations on the method to be used to introduce
these components containing functional groups into olefin compounds,
an olefin compound to be used as major component may be copolymerized
first with an olefin compound containing a functional group, or
an unmodified polyolefin may be graft-copolymerized with an olefin
compound containing a functional group using a radical initiator.
Such a component containing a functional group to be introduced
should preferably account for 0.001-40 mol%, more preferably 0.01-35
mol%, of the entire olefin monomers in the modified polyolefin.
[0018]

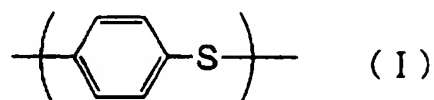
With no particular limitations on the method to be used to produce
said (a) polyolefin resin, there are many useful processes including
radical polymerization, coordination polymerization using a
Ziegler-Natta catalyst, anionic polymerization, and coordination
polymerization using a metallocene catalyst.

[0019]

Said (b) PPS resin to be used for the present invention is a polymer
that comprises repeating units as shown by the following structural
formula (1): [Chemical formula (1)], and to achieve a high heat
resistance, said polymer component comprising repeating units as
represented by the above structural formula should preferably

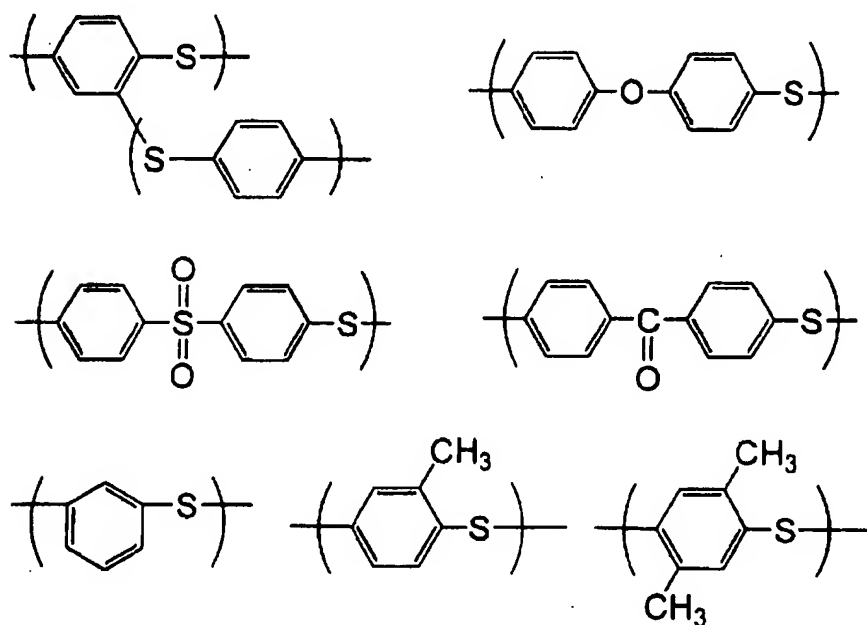
account for 70 mol% or more, more preferably 90 mol% or more, of the entire polymer.

[Chemical formula (1)]



In said PPS resin, repeating units as represented by the following structural formula may account for less than 30 mol% or so of all repeating units.

[Chemical formula (2)]



[0020]

PPS polymers that partly consist of such a structure generally have a low melting point, so if thermoplastic resin with a low melting point is used as material for the non-barrier layer in the laminated structure according to the invention, said polymers are advantageous in terms of moldability.

[0021]

Though there are no specific limitations on the melt viscosity of a PPS polymer to be used for the present invention as long as kneading of the melt can be performed, it is generally in the range of 50-20000 poise (320°C, shearing speed 1000 sec⁻¹), more preferably 100-5000 poise.

[0022]

Such PPS resins are generally produced by known methods including the process for production of polymers with a relatively small molecular weight described in Japanese Examined Patent Applications Publication (Kokoku) SHO 45-3368, and the processes for production of polymers with a relatively large molecular weight described in Japanese Examined Patent Applications Publication (Kokoku) SHO 52-12240 and Japanese Patent Laid-Open Publication (Kokai) SHO 61-7332. For purposes of the invention, PPS resins as produced above, as a matter of course, may be subjected, before use, to different treatment processes including crosslinking and chain extension by heating in air, heat treatment in an inert gas atmosphere such as nitrogen or under reduced pressure, washing with an organic solvent, hot water or an acid solution, and activation with compounds containing a functional group such as acid anhydrides, amine, isocyanates, and disulfide compounds containing a functional group.

[0023]

Specifically, crosslinking or chain extension of PPS resin by heating can be performed in an atmosphere of an oxidizing gas such as air and oxygen, or in an atmosphere of a mixture of said oxidizing gas and an inert gas such as nitrogen and argon, in a heating container where the resin is heated at an appropriate temperature until a required melt viscosity is achieved. Heating is usually performed at a temperature of 170-280°C, more preferably 200-270°C, for a period of 0.5-100 hours, more preferably 2-50 hours, in most cases,

but the two parameters may be controlled appropriately to achieve a required viscosity. Equipment used for said heating may be a hot air dryer or a rotation type or stirrer type heating system, of which rotation type or stirrer type heating equipment is preferred to ensure efficient, uniform processing.

[0024]

Specifically, heating of PPS resin in an inert gas atmosphere such as nitrogen or under reduced pressure may be performed by heating the resin in an inert gas atmosphere such as nitrogen or under reduced pressure at a heating temperature of 150-280°C, more preferably 200-270°C, for a heating time of 0.5-100 hours, more preferably 2-50 hours. Equipment used for said heating may be a hot air dryer or a rotation type or stirrer type heating system, of which rotation type or stirrer type heating equipment is preferred to ensure efficient, uniform processing.

[0025]

PPS resin used for the present invention should preferably be deionized before use. Said deionization may be carried out by washing with an acid solution, washing with hot water, or washing with organic solvent, which may be performed in combination.

[0026]

The following methods can be used for washing PPS resin with an organic solvent. There are no specific limitations on the organic solvent to be used for washing of PPS resin unless it has unfavorable effects such as decomposition of the PPS resin, and preferred ones include: nitrogen-containing polar solvents including N-methylpyrrolidone, dimethylformamide, and dimethylacetamide; sulfoxide- or sulfone-based solvents including dimethylsulfoxide and dimethylsulfone; ketone-type solvents including acetone, methyl ethyl ketone, diethyl ketone, and acetophenone; ether-type solvents

including dimethyl ether, dipropyl ether, and tetrahydrofuran; halogen-based solvents including chloroform, methylene chloride, trichloroethylene, ethylene dichloride, dichloroethane, tetrachloroethane, and chlorobenzene; alcohol- and phenol-type solvents including methanol, ethanol, propanol, butanol, pentanol, ethylene glycol, propylene glycol, phenol, cresol, and polyethylene glycol; and aromatic hydrocarbon type solvents including benzene, toluene, and xylene. Of the above organic solvents, preferred ones include N-methylpyrrolidone, acetone, dimethylformamide, and chloroform. These organic solvents may be used solely or in combination. Washing with an organic solvent may be carried out by immersion of PPS resin in the organic solvent, while stirring or heating it as required. There are no specific limitations on the washing temperature used to wash PPS resin with an organic solvent, and an appropriate temperature may be selected in the range from room temperature to about 300°C. The efficiency of washing generally increases with the washing temperature, but normally, required effect of washing is achieved at a washing temperature in the range of room temperature to 150°C. After the completion of washing with an organic solvent, the PPS resin should preferably be rinsed several times with warm water to remove the residual organic solvent.

[0027]

Hot water treatment of PPS resin can be carried out by the following methods. To achieve desired chemical modification of PPS resin by hot water washing, water to be used should preferably be either distilled water or deionized water. Hot water treatment is normally performed by putting an appropriate amount of PPS resin in an appropriate amount of water, followed by heating and stirring under atmospheric pressure or in a pressure vessel. The amount of water should preferably be larger than that of PPS resin, and normally,

one liter of water is used for every 200g or less of PPS resin in the bath.

[0028]

Acid treatment of PPS resin can be carried out by the following methods. Specifically, such treatment may be carried out by immersion of PPS resin in an acid or an acid solution, while stirring or heating it as required. There are no specific limitations on the acid to be used unless it works to decompose the PPS resin, and preferred ones include: saturated aliphatic monocarboxylic acids including formic acid, acetic acid, propionic acid, and butyric acid; halogen-substituted saturated aliphatic carboxylic acids including chloroacetic acid and dichloroacetic acid; unsaturated aliphatic monocarboxylic acids including acrylic acid and crotonic acid; aromatic carboxylic acids including benzoic acid and salicylic acid; dicarboxylic acids including oxalic acid, malonic acid, succinic acid, phthalic acid, and fumaric acid; and inorganic acid compounds including sulfuric acid, phosphoric acid, hydrochloric acid, carbonic acid, and silicic acid. Among others, acetic acid and hydrochloric acid are preferred. Acid treated PPS resin should preferably be washed several times with water or warm water to remove the residual acids and salts. Distilled water or demineralized water should preferably be used for the washing process to avoid impairment of desired modification by the acid treatment in the PPS resin.

[0029]

In the laminated structure according to the invention, a known conventional compatibilizer may be added with the aim of improving the compatibility between the polyolefin resin used as component (a) and the PPS resin used as component (b). Specifically, useful compatibilizers include: alkoxysilane and other organosilanes comprising at least one functional group selected from the group

consisting of epoxy, amino, isocyanate, hydroxyl, mercapto, and ureido; random, block and graft copolymers and other modified polyolefins consisting of an α -olefin, such as ethylene and propylene, in combination with at least one compound selected from the group consisting of α , β -unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, and crotonic acid, and derivatives thereof such as esters, anhydrides, halides, sodium salts, potassium salts, magnesium salts, and zinc salts thereof; epoxy-containing olefin-based copolymers and multifunctional epoxy compounds, such as olefin-based copolymers consisting mainly of an α -olefin and a glycidyl ester of an α , β -unsaturated acid; which may be used in combination.

[0030]

In the laminated structure according to the invention, the polyolefin resin used as component (a) and the PPS resin used as component (b) should account for 5-80 vol% and 95-20 vol%, respectively, in order to produce a desired phase structure (for instance, a sea-island structure) wherein the PPS resin component forms a continuous phase (matrix phase) while the polyolefin resin component forms a dispersion phase. Here, if the PPS resin accounts for a smaller portion, such as in a structure consisting of 55-80 vol% polyolefin resin and 45-20 vol% PPS resin, a barrier layer comprising a continuous phase of the PPS resin can be produced by appropriately controlling the melt viscosity ratio between the polyolefin resin and the PPS resin. A barrier layer comprising said phase structure is particularly preferred because it can achieve a good balance among toughness, interlayer adhesion, barrier properties and required costs. Further, said polyolefin resin and said PPS resin should more preferably account for 60-75 vol% and 40-25 vol%, respectively, while maintaining a phase structure as described above. If said

polyolefin resin used as component (a) accounts for more than 80 vol%, the PPS resin component cannot form a continuous phase that characterizes the laminated structure according to the invention, making it impossible to achieve the goal of the invention. If said polyolefin resin accounts for less than 5 vol%, on the other hand, the interlayer adhesion in the laminated structure will decrease, resulting in undesirable results.

[0031]

To produce a phase structure (for instance, a sea-sea structure) consisting of a PPS resin component and a polyolefin resin component, each forming a virtually continuous phase (matrix phase), it is important to control the melt viscosity and compatibility of the polyolefin resin and the PPS resin in the composition range of 15-85 vol% polyolefin resin and 85-15 vol% PPS resin. To produce a phase structure as described above by controlling the melt viscosity and compatibility of the two components, the composition should preferably be in the range of 30-70 vol% polyolefin resin and 70-30 vol% PPS resin, more preferably 35-65 vol% polyolefin resin and 65-30 vol% PPS resin. If said polyolefin resin used as component (a) accounts for more than 85 vol%, the PPS resin component cannot form a virtually continuous phase, making it impossible to achieve the goal of the invention. If said polyolefin resin used as component (a) accounts for less than 15 vol%, on the other hand, it will be difficult for the polyamide resin component to form a virtually continuous phase.

[0032]

To allow the polyolefin resin component to form a continuous phase (matrix phase) while allowing the PPS resin component to form a zonal dispersion phase (laminar structure), the composition should preferably be in the range of 55-95 vol% polyolefin resin and 45-5

vol% PPS resin, more preferably 60-90 vol% polyolefin resin and 40-10 vol% PPS resin. If the polyolefin resin used as component (a) accounts for more than 95 vol%, it will be difficult for the PPS resin component to form a zonal dispersion phase with a sufficient length and size and to achieve sufficiently enhanced barrier properties, making it impossible to achieve the goal of the invention. If the polyolefin resin used as component (a) accounts for less than 55 vol%, on the other hand, it will be difficult for the polyamide resin to form a zonal dispersion phase.

[0033]

In the laminated structure according to the invention, the adjacent layer (B) to either side of the barrier layer should preferably comprise a thermoplastic resin different from the resin that forms the barrier layer. There are no limitations on the thermoplastic resin to be used, and it is possible to select suitable ones to suit the objectives of the laminated structure, said suitable ones including saturated polyester resin, polysulfone resin, polytetrafluoroethylene, polyetherimide resin, polyamide imide resin, polyamide resin, polyimide resin, polycarbonate resin, polyethersulfone resin, polyether ketone resin, polythioether ketone resin, polyether ether ketone resin, thermoplastic polyurethane resin, polyolefin resin, ABS resin, polyamide elastomer, and polyester elastomer, which may be used in combination as a mixture. Among others, polyolefin resin, thermoplastic polyester resin, polyamide resin, polycarbonate resin, and ABS resin are preferred.

[0034]

Said preferred polyolefin resins used here include the same as said polyolefin resins to be used as component (a), but among others, lower, medium or high density polyethylene, polypropylene, ethylene/propylene copolymer, poly(1-butene), poly(4-methyl

pentynes-1), chlorinated polyethylene, and chlorinated polypropylene are preferred.

[0035]

Said preferred thermoplastic polyester resins refer to those polyesters which are produced from a dicarboxylic acid, such as terephthalic acid, and an aliphatic diol. Preferred dicarboxylic acids other than terephthalic acid include: aliphatic dicarboxylic acids with 2-20 carbon atoms such as azelaic acid, sebacic acid, adipic acid, and decane dicarboxylic acid; aromatic dicarboxylic acids such as isophthalic acid and naphthalene dicarboxylic acid; alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid, which may be used solely or in combination. Preferred aliphatic diols include ethylene glycol, 1,2-propylene glycol, 1,4-butanediol, trimethylene glycol, 1,4-cyclohexanedimethanol, and hexamethylene glycol.

[0036]

Preferred thermoplastic polyesters for the present invention include polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polyhexamethylene terephthalate, polycyclohexylene dimethylene terephthalate, and polyethylene naphthalate, but particularly preferred are copolyesters consisting of a 1,4-butanediol component and a dicarboxylic acid component that contains 60 mol% or more, preferably 70 mol% or more, of either polybutylene terephthalate, which has moderate mechanical strength, or terephthalic acid, and dodecane dicarboxylic acid and/or isophthalic acid.

[0037]

There are no limitations on the degree of polymerization of said thermoplastic polyester resins, but in the case of polybutylene terephthalate and copolyesters, which are used frequently, the

degree of polymerization should preferably be such that the relative viscosity as determined in 0.5% orthochlorophenol solution at 25°C is in the range of 0.5-2.5, more preferably 0.8-2.0. In the case of polyethyleneterephthalate, the intrinsic viscosity as determined in 5% orthochlorophenol solution at 25°C should preferably be in the range of 0.54-1.5, more preferably 0.6-1.2.

[0038]

Said preferred polyamide resins include polyamides consisting mainly of amino acid, lactam or diamine, in combination with a dicarboxylic acid. Compounds frequently used as said main components include: amino acids such as 6-aminocaproic acid, 11-amino undecanoic acid, 12-amino dodecane acid, and para-aminomethyl benzoic acid; lactams such as ϵ -caprolactam and ω -laurolactam; aliphatic, alicyclic, and aromatic diamines such as tetramethylenediamine, hexamethylenediamine, 2-methylpentamethylenediamine, nonamethylenediamine, undecamethylenediamine, dodecamethylenediamine, 2,2,4-/2,4,4-trimethylhexamethylenediamine, 5-methylnonamethylenediamine, metaxylylenediamine, paraxylylenediamine, 1,3-bis(aminomethyl)cyclohexane, 1,4-bis(aminomethyl)cyclohexane, 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane, bis(4-aminocyclohexyl)methane, bis(3-methyl-4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)propane, bis(aminopropyl)piperazine, and aminoethylpiperazine; aliphatic, alicyclic, and aromatic dicarboxylic acids such as adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedionic acid, terephthalic acid, isophthalic acids, 2-chloroterephthalic acid, 2-methyl terephthalic acids, 5-methylisophthalic acid, 5-sodium sulfoisophthalic acid,

hexahydroterephthalic acid, and hexahydroisophthalic acid; and for the present invention, nylon homopolymers and copolymers derived therefrom can be used solely or in combination as a mixture.

[0039]

Particularly useful polyamide resins for the present invention are those having high heat resistance, high strength, and a melting point of 150°C or above, including polycaproamide (nylon 6), polyhexamethylene adipamide (nylon 66), polycaproamide/polyhexamethylene adipamide copolymer (nylon 6/66), polytetramethylene adipamide (nylon 46), polyhexamethylene sebacamide (nylon 610), polyhexamethylene dodecamide (nylon 612), polyhexamethylene terephthalamide/polycaproamide copolymer (nylon 6T/6), polyhexamethylene adipamide/polyhexamethylene terephthalamide copolymer (nylon 66/6T), polyhexamethylene adipamide/polyhexamethylene isophthalamide copolymer (nylon 66/6I), polyhexamethylene adipamide/polyhexamethylene terephthalamide/polyhexamethylene isophthalamide copolymer (nylon 66/6T/6I), polyhexamethylene terephthalamide/polyhexamethylene isophthalamide copolymer (nylon 6T/6I), polyhexamethylene terephthalamide/polydodecaneamide copolymer (nylon 6T/12), polyhexamethylene terephthalamide/poly(2-methylpentamethylene) terephthalamide copolymer (nylon 6T/M5T), polyxylylene adipamide (nylon XD6), polynonamethylene terephthalamide (nylon 9T), and mixtures and copolymers thereof.

[0040]

Particularly preferred ones include nylon 6, nylon 66, nylon 12, nylon 11, and nylon 6/66 copolymer, and nylon 610; and copolymers containing hexamethylene terephthalamide units such as nylon 6T/66 copolymer, nylon 6T/6I copolymer, and nylon 6T/6 copolymer, and

in practical applications, these polyamide resins may be used in combination as a mixture to achieve required moldability, heat resistance and barrier properties.

There are no specific limitations on the polymerization degree of these polyamide resins, but normally, the relative viscosity as determined in 1%-content 98% concentrated sulfuric acidic solution at 25°C should preferably be in the range of 2.0-7.0, more preferably 2.5-6.0.

[0041]

Thermoplastic resin that forms said adjacent layer (B) may contain additives, such as plasticizer, antioxidant, nucleating agent and coloring agent, that are suitable for the resin.

[0042]

A film type or sheet type laminated structure that consists of a barrier layer having a phase structure as defined for the invention and an adjacent layer to either side thereof, may be produced by melting the compositions for the layers in separate extruders, supplying them to a multilayer die, and coextruding them into said barrier layer with a specific phase structure and said adjacent layer of thermoplastic resin; or by forming the adjacent layer of thermoplastic resin, followed by melt extrusion into said barrier layer, by the so-called laminate molding process. Conventional coextrusion methods can be used to produce a laminated structure in the form of a hollow container, such as bottle, barrel and tank, or a tubular product, such as pipe and tube, and for instance, a two-layer hollow product consisting of an inner barrier layer having a specific phase structure and an outer thermoplastic resin layer may be produced by supplying a resin composition for said barrier layer and a thermoplastic resin composition into two separate extruders, the two separately-extruded flows of molten resins then

being supplied into a die under pressure, shaped into rings and combined in the die to form an inner layer of said resin composition for the barrier and an outer thermoplastic resin layer, followed by coextrusion thereof out of the die and tubing or blowing by an conventional process. In the case of three-layer hollow moldings, three layers can be formed by the same procedure as described above using three extruders, or two-resin, three-layer hollow products can be produced using two extruders. Among others, the coextrusion molding method is preferred because strong interlayer adhesion can be achieved.

[0043]

In producing a laminated product as described above, an adhesive layer (C) may be provided between other layers to enhance the strength of adhesion between them. There are no specific limitations on the structure of the material to be used for the adhesive layer as long as it can serve to adhere the thermoplastic resin layer to the barrier layer consisting of polyolefin resin and PPS resin, and can be coextruded with them. Specifically, useful materials include: random, block and graft copolymers and other modified polyolefins consisting of an α -olefin, such as ethylene and propylene, in combination with at least one compound selected from the group consisting of α,β -unsaturated carboxylic acids, such as acrylic acid, methacrylic acid, maleic acid, and crotonic acid, and derivatives thereof such as esters, anhydrides, halides, sodium salts, potassium salts, magnesium salts, and zinc salts thereof; random, block and graft copolymers consisting of an α -olefin, such as ethylene and propylene, in combination with at least one compound selected from the group consisting of vinyl acetate, vinyl alcohol, and styrene; copolyamide type adhesives; and copolyester type adhesives. Thus, by using such adhesive layers in different ways,

the laminated structure according to the invention can be in the form of a two-resin, two-layer product, a two-resin, three-layer product, a three-resin, three-layer product, a three-resin, four-layer product, or a three-resin, five-layer product.

[0044]

For purposes of the present invention, a fibrous or non-fibrous filler may be added as required to the resins that form layers of the laminated structure. Specifically, materials that can be used for said fibrous or non-fibrous filler include fibrous ones such as glass fiber, carbon fiber, potassium titanate whisker, zinc oxide whisker, alumina fiber, silicon carbide fiber, ceramic fiber, asbestos fiber, gypsum fiber, and metallic fiber; silicates such as wollastonite, sericite, kaolin, mica, clay, bentonite, asbestos, talc, and alumina silicate; expansive sheet silicates such as montmorillonite and synthetic mica; metallic compounds such as alumina, silicon oxide, magnesium oxide, zirconium oxide, titanium oxide, and iron oxide; carbonates such as calcium carbonate, magnesium carbonate, and dolomite; sulfates such as calcium sulfate and barium sulfate; and other non-fibrous fillers such as glass bead, ceramic bead, boron nitride, silicon carbide, calcium phosphate, and silica; which may be in a hollow form and may be used in combination.

To achieve high mechanical strength and good barrier properties, it is preferred to perform preliminary treatment of said fibrous or non-fibrous fillers with coupling agents such as isocyanate compounds, organosilane compounds, organotitanium compounds, organoborane compounds, and epoxides, while preliminary treatment with organic onium ions may be effective when an expansive sheet silicates is used.

[0045]

For purposes of the invention, other ordinary additives including antioxidant, thermal stabilizer, lubricant, plasticizer, crystal nucleation agent, anti-ultraviolet agent, coloring agent, and flame retardant may be added to layers in the laminated structure, unless they prevent the product from meeting the goal of the including or having desired effects. Further, the laminated structure according to the invention may contain resins such as polyphenylene oxide, polysulfone, polytetrafluoroethylene, polyetherimide, polyamide imide, polyimide, polycarbonate, polyethersulfone, polyether ketone, polyether ether ketone, epoxy resin, phenol resin, polyethylene, polystyrene, polypropylene, ABS resin, polyester, polyamide elastomer, and polyester elastomer, in addition to the main components of the resins that form the layers in the laminated structure according to the invention, unless they prevent said laminated structure from having desired effects.

[0046]

Laminated structures that are produced according to the invention have good gas barrier properties, chemical resistance, moisture permeability and moldability, and serve effectively as containers for transportation and storage of oil, gasoline and other liquid chemicals, and packages and containers for foods and medical products.

[0047]

The present invention is described more in detail below by using examples.

[Examples]

The properties referred to in the examples and comparative examples were measured by the following methods.

(1) Observation of the phase structure: The cross section of the barrier layer in a tube was observed by scanning electron microscopy

(SEM) .

(2) Gasohol barrier properties: A 30 cm piece was cut out of the tube, and after closing one end, filled with an alcohol gasoline blend consisting of 85:15 (weight ratio) of commercial regular-class gasoline and methyl alcohol, followed by closing the other end. Subsequently, the filled tube was weighed, and placed in an explosion proof type oven adjusted to 40°C, followed by evaluation of the gas barrier properties against the alcohol gasoline blend based on changes in weight.

(3) Interlayer adhesion strength of molded product: A 10 mm wide rectangular piece was cut out of the tube, and the inner and outer layers on either side of the adhesive layer (which was adhered to the adjacent layer that comprised a thermoplastic resin composition) were pulled in the opposite directions, followed by determination of the adhesion strength per unit length.

[0048]

[Reference example 1 (production of copolymerized PPS)]

A 3.26 kg amount of sodium sulfide (25 moles, containing 40% of water of crystallization), 4 g of sodium hydroxide, 1.36 kg (about 10 moles) of sodium acetate trihydrate, and 7.9 kg of N-methylpyrrolidone were put in an autoclave equipped with a stirrer, and heated gradually up to 205°C while stirring, followed by removal of 1.5 liters of distillate water including 1.36 kg of water. A 3.38 kg amount (23.0 moles) of 1,4-dichlorobenzene, 0.37 kg (2.5 moles) of 1,3-dichlorobenzene, and 2 kg of NMP were added to the residual mixture, and heated for 5 hours at 265°C. The reaction product was washed three times with hot water at 70°C, washed with acetic acid solution with a pH of 4 at 60°C, washed four times with hot water at 70°C, and then dried under reduced pressure for 24 hours at 80°C to produce 2 kg of copolymerized PPS resin with a

melting point of 255°C and melt flow rate (MFR) of about 800g per 10 min (315°C, under a load of 5000g).

[0049]

<polyolefin resin>

(PO-1): High density polyethylene with a melt index (MI) of 0.3 and a density of 0.95.

(PO-2): High density polyethylene with a MI of 6.0 and a density of 0.96.

(PO-3): Low density polyethylene of a MI of 1.0 and a density of 0.92.

(PO-4): Polypropylene with a MI of 0.5 and a density of 0.89.

(PO-5): Ethylene-ethylacrylate copolymer with a MI of 1.5 and a density of 0.93.

(PO-6): Ethylene-propylene copolymer with a MI of 0.6 and a density of 0.88.

<PPS resin>

(PPS-1): PPS resin with a melting point of 280°C and a melt flow rate (MFR) of 100g per 10 min (315°C, under a load of 5000g).

(PPS-2): PPS resin with a melting point of 280°C and a MFR of 600g per 10 min.

(PPS-3): Copolymerized PPS resin with a melting point of 255°C and a MFR of 800g per 10 min, produced in the above-mentioned reference example.

[0050]

<Thermoplastic resin other than the resin composition forming the barrier layer>

(B-1): High density polyethylene with a MI of 0.3 and a density of 0.94.

(B-2): Polybutylene terephthalate (Lumicon 5201X11, supplied by Toray Industries, Inc.).

(B-3): Nylon 11 (Rilsan BESN O P40TL, supplied by Toray Industries, Inc.).

<Adhesive layer>

(C-1): 90/10 (wt%) ethylene/glycidylmethacrylate copolymer.

(C-2): 64/30/6 (wt%) ethylene/methylacrylate/glycidylmethacrylate copolymer.

[0051]

[Examples 1-9, comparative examples 1-3]

As shown in Tables 1 and 2, PPS resin and a compatibilizer (90/10 (wt%) ethylene/glycidylmethacrylate copolymer) were mixed, supplied through the main feeder of a Japan Steel Works TEX30 biaxial extruder, while supplying polyolefin resin through a side feeder to a mid portion of the cylinder, followed by melt kneading at a kneading temperature of 270-300°C and a screw revolution speed of 200 rpm. The pellet produced were dried, and supplied to a tube molding process.

A three-resin, three-layer tube was molded, which consisted of a barrier layer (A) comprising the composition produced above, an adjacent layer (B) comprising thermoplastic resin, and an adhesive layer (C) existing between the barrier layer and the adjacent layer. The molding equipment used consisted of three extruders, a die to mold a tube from the resins discharged from the three extruders and collected by an adapter, a sizing die to cool the tube and control its size, and take-up equipment.

The three-layer tube obtained had an outside diameter of 8 mm, inside diameter of 6 mm, outside layer (thermoplastic resin layer) thickness of 0.70 mm, adhesive layer thickness of 0.10 mm, and inside layer (barrier layer) thickness of 0.20 mm. Results of evaluation of this multilayer tube are shown in Tables 1 and 2.

[0052]

[Table 1]

	Items	Unit	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Barrier layer components, Layer (A)	Type of polyolefin resin (a) Proportion of polyolefin resin	- vol%	PO-1 65	PO-2 50	PO-2 77	-	PO-2 70	PO-1 100
	Type of PPS resin (b) Proportion of PPS resin	- vol%	PPS-2 30	PPS-2 45	PPS-1 20	PPS-1 100	PPS-1 25	-
	Ethylene/glycidylmethacrylate copolymer	vol%	5	5	3	-	5	-
Layer (B)	Thermoplastic resin layer		B-1	B-1	B-1	B-1	B-1	B-1
Layer (C)	Adhesive layer		C-1	C-1	C-1	C-1	C-1	C-1
Phase structure of barrier layer			PPS matrix	PPS/ polyolefin matrix	PPS zonal distribution	PPS matrix	Polyolefin matrix	Polyolefin matrix
Gasohol barrier properties	Gasohol permeability (g·mm/m ² ·24h·atm)		0.67	0.75	0.89	0.24	10 or more	10 or more
Interlayer adhesion strength in moldings (kg/10mm)			3.1	3.5	4.2	0.5 or less	not separated	not separated

<Polyolefin resin>

(PO-1): High density polyethylene with a MI of 0.3 and a density of 0.95.

(PO-2): High density polyethylene with a MI of 6.0 and a density of 0.96.

<PPS resin>

(PPS-1): PPS resin with a melting point of 280°C and a MFR of 100g/10min

(PPS-2): PPS resin with a melting point of 280°C and a MFR of 600g/10min

<Thermoplastic resin other than the resin composition forming the barrier layer>

(B-1): High density polyethylene with a MI of 0.3 and a density of 0.94.

<Adhesive layer>

(C-1): Ethylene/glycidylmethacrylate copolymer

[0053]

[Table 2]

	Items	Unit	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Barrier layer components Layer (A)	Type of polyolefin resin (a) Proportion of polyolefin resin	- vol%	PO-3 40	PO-4 80	PO-5 55	PO-6 77	PO-1 65	PO-1 65
	Type of PPS resin (b) Proportion of PPS resin	- vol%	PPS-2 60	PPS-3 15	PPS-3 40	PPS-3 20	PPS-3 30	PPS-2 30
	Ethylene/glycidylmethacrylate copolymer	vol%	5	5	5	3	5	5
Layer (B)	Thermoplastic resin layer		B-1	B-1	B-2	B-3	B-2	B-3
Layer (C)	Adhesive layer		C-1	C-1	C-1	C-2	C-1	C-2
Phase structure of barrier layer			PPS matrix	PPS zonal distribution	PPS/polyolefin matrix	PPS/polyolefin matrix	PPS matrix	PPS matrix
Gasohol barrier capability	Gasohol permeability (g·mm/m ² ·24h·atm)		0.54	0.82	0.63	0.75	0.70	0.56
Interlayer adhesion strength in moldings (kg/10mm)			2.6	4.7	4.5	4.4	3.9	3.8

<Polyolefin resin>

(PO-1): High density polyethylene with a MI of 0.3 and a density of 0.95.

(PO-3): Low density polyethylene of a MI of 1.0 and a density of 0.92.

(PO-4): Polypropylene with a MI of 0.5 and a density of 0.89.

(PO-5): Ethylene-ethylacrylate copolymer with a MI of 1.5 and a density of 0.93.

(PO-6): Ethylene-propylene copolymer with a MI of 0.6 and a density of 0.88.

<PPS resin>

(PPS-2): PPS resin with a melting point of 280°C and a MFR of 600g/10 min.

(PPS-3): Copolymerized PPS resin with a melting point of 255°C and a MFR of 800g/10min

<Thermoplastic resin other than the resin composition forming the barrier layer>

(B-1): High density polyethylene with a MI of 0.3 and a density of 0.94.

(B-2): Polybutylene terephthalate.

(B-3): Nylon 11.

<Adhesive layer>

(C-1): Ethylene/glycidylmethacrylate copolymer.

(C-2): Ethylene/methylacrylate/glycidylmethacrylate copolymer.

[0054]

The laminated structures having the phase structure according to the present invention that were produced in examples 1-9 had good barrier properties and a strong interlayer adhesion, indicating that they had high practicability.

[0055]

[Effect of invention]

The laminated structure according to the invention serves to produce plastic containers and tubular products that have a high strength, durability, and moldability, as well as high good gasohol barrier properties, which serve effectively as gasoline tanks for automobiles, containers for transportation storage of liquid chemicals, pipes, and packages and containers for foods and medical products.



[Title of the document] Abstract

[Abstract]

[Problem]

To provide a laminated structure that serves to produce plastic containers and tubular products with a high strength, durability, and moldability, as well as good gasohol barrier properties.

[Means of solving the problem]

A laminated structure comprising at least one barrier layer of a resin composition consisting of polyolefin resin and polyphenylene sulfide resin mixed at a specific ratio, wherein the resin phase structure as observed by electron microscopy comprises a continuous layer of polyphenylene sulfide resin or a zonal distribution layer of polyphenylene sulfide resin.

[Selected drawings]

None